The Hydrogen Fluoride Solvent System. Part VI.[1] Solutions of Hydrogen Cyanide, Silver(I) Cyanide, and Hexacyanoferric(II) Acid: Formation of the Difluoromethylammonium Cation

By **Ronald J. Gillespie** * and **Roger Hulme**, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

Hydrogen cyanide, a non-electrolyte in anhydrous hydrogen fluoride, is protonated in the presence of boron trifluoride and arsenic pentafluoride. Unstable solids believed to be $HCNH^+BF_4^-$ and $HCNH^+AsF_6^-$ have been prepared. In solution in hydrogen fluoride, hydrogen cyanide slowly adds HF to form the cation $F_2HC{\cdot}NH_3^+$, which has been isolated as the AsF_6^- salt. Further slow reaction occurs in solution to form a polymer containing $CF_2H{\cdot}NH$ groups. Conductimetric titrations of silver(I) cyanide and hexacyanoferric(II) acid with BF_3 show that neither solute liberates HCN in this solvent; hexacyanoferric(II) acid forms $Fe(HCN)_6^{2+}$.

KLATT'S[2] report that alkali-metal cyanides are completely solvolysed by anhydrous hydrogen fluoride to liberate HCN, has caused other authors to describe HCN as insoluble in HF. Dove and Hallett,[3] however, found that HCN and HF are completely miscible at 20 °C but the solutions are unstable, the characteristic i.r. band of HCN at 2138 cm^{-1} disappearing with a half-life of about 40 h at room temperature. The work on HCN solutions in HF described in this paper was initially prompted by a need for a more complete knowledge of the behaviour of these solutions in order to interpret our data on HF solutions of other cyano-complexes, particularly those of mercury(II) cyanide.[4]

We have also made some investigations on solutions of silver(I) cyanide, a solute which Klatt found to be

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[1] Part V, M. Brownstein and R. J. Gillespie, *J.C.S. Dalton*, 1973, 67.

[2] W. Klatt, *Z. phys. Chem.* (*Leipzig*), 1939, **A185**, 306.

[3] M. F. A. Dove and J. G. Hallett, *J. Chem. Soc.* (*A*), 1969, 2781.

[4] R. J. Gillespie, R. Hulme, and D. A. Humphreys, *J. Chem. Soc.* (*A*), 1971, 3574.

insufficiently soluble for ebullioscopic measurements. Dove and Hallett[3] have shown that, on dissolution in HF, silver(I) cyanide gives rise to an equilibrium mixture of $Ag(NCH)_n^+$ ($n = 1$ or 2), Ag^+, and HF_2^-. Olah and Kiorsky[5] have demonstrated that silver(I) cyanide liberates HCN in fluorosulphuric acid containing antimony pentafluoride to form $HCNH^+$, which was identified by means of its proton n.m.r. spectrum.

Schilt[6] reported that the complex (1,10-phenanthroline)$_2$Fe(CN)$_2$] is dibasic in sulphuric acid and suggested that cyano-complexes of this type undergo protonation on the metal atom. However, there is now good evidence that protonation of the nitrogen of the M–C–N system occurs.[7] The fact that complexes of the type $[L_nFe(CN)_{6-n}]$[8] will, in acidic media, add a number of protons equal to the number of cyano-groups suggested the possibility that hexacyanoferric(II) acid would show basic properties in anhydrous hydrogen fluoride.

RESULTS AND DISCUSSION

Solutions of Hydrogen Cyanide.—Contrary to the report of Klatt, but in accord with the observations of Dove and Hallett,[3] we found HCN to be miscible with HF to give very weakly conducting solutions. Thus, HCN is, at the most, a very weak base in this solvent and is probably a non-electrolyte. This is confirmed by the i.r. spectrum of the solution which shows no absorption characteristic of HF_2^- in the 1600 cm^{-1} region.[3] The proton n.m.r. spectrum of the solution showed only one absorption, other than that due to the solvent, with a shift of 226 Hz below external TMS and a width at half-height of *ca.* 3 Hz. The peak-width was unaffected by cooling to −85 °C, but could be reduced to *ca.* 0·5 Hz by irradiating the ^{14}N nucleus at 4·4 MHz. This strongly suggests that the line-width is due solely to incomplete relaxation of the quadrupole ^{14}N nucleus and not to unresolved coupling to a short-lived proton on the nitrogen atom. Carbon-13 satellites, J 282 Hz, have been observed[3] for the HCN absorption, thus putting a lower limit of 4×10^{-3} s on the life-time of the proton attached to the carbon atom; this is in accord with the expected non-acidic properties of the HCN molecule in this solvent. Nevertheless, Dove and Hallett found that a solution of HCN in DF showed an i.r. band due to DCN. Since kinetically significant amounts of free cyanide ion are unlikely to exist, the exchange probably proceeds *via* the ion $HCNH^+$ which Olah and Kiorsky[5] have observed in very highly acidic systems. We found that the proton n.m.r. spectra of solutions of $HC^{15}N$ in HF showed a doublet, J 11·5 Hz, having a line-width of *ca.* 0·5 Hz. This confirms that the width of the $HC^{14}N$ signal arises from incomplete quadrupole relaxation. The observed value of $J_{^{15}N-C-H}$ differs markedly from that found for the neat liquid[9] (8·7 Hz), and from that in $HC^{15}NH^+$ ($J_{HC^{15}N}$ 19·0 Hz). The increase in the H–^{15}N coupling from neat HCN through HCN in HF to $HNCH^+$ is consistent with the supposition that increased interaction of the nitrogen lone-pair with a hydrogen atom through hydrogen bonding or, in the limit, protonation, increases the p character of the lone-pair orbital and thus the s character of the N–C bond.

TABLE 1

Conductimetric titrations of HCN and AgCN in HF with BF_3 at 0 °C

[HCN] = 0·457 mol kg^{-1}		[AgCN] = 0·256 mol kg^{-1}	
Mole ratio BF_3 : HCN	$10^2\kappa$ / Ω^{-1} cm^{-1}	Mole ratio BF_3 : AgCN	$10^2\kappa$ / Ω^{-1} cm^{-1}
0·00	0·24	0·0	6·02
0·11	1·44	0·21	5·52
0·16	1·84	0·45	4·98
0·43	3·78	0·76	4·00 †
0·63	4·70	0·95	3·43 †
0·82	4·98	1·21	3·43 †
1·02	5·13	2·22	3·68 †
1·64	5·13	3·0	3·80 †

† White precipitate present.

Addition of the very weak electrolyte BF_3 to a solution of HCN in HF resulted in a sharp rise in conductivity (Table 1 and Figure 1). Complexing of the fluoride ion with BF_3 causes equilibrium (1) to shift far to the right.

$$HCN + HF \rightleftharpoons HCNH^+ + F^- \qquad (1)$$

Initially the conductivity of these solutions was almost identical with that of solutions of the strong electrolyte KBF_4 at the same concentrations.[10] In the presence of an excess of HCN, the added BF_3 was converted essentially quantitatively to $HCNH^+BF_4^-$, but as the BF_3 : HCN ratio increased, the extent of ionization diminished and the conductivity fell below that of KBF_4. Clearly, HCN is not a strong base even in the highly acidic medium HF–BF_3. We were unable to observe the

$$HCN + HF + BF_3 \rightleftharpoons HCNH^+ + BF_4^- \quad (2)$$

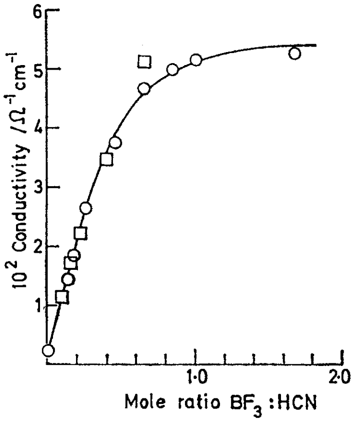

FIGURE 1 Conductimetric titration of HCN in HF (0·453 mol kg^{-1}) with BF_3 at 0 °C: (○), HCN–BF_3; (□), KBF_4 at the same concentration as that of BF_3 (ref. 10)

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[5] G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, 1968, **90**, 4666.

[6] A. A. Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 5779.

[7] G. Wilkinson, 'Advances in Chemistry of the Coordination Compounds,' ed. S. Kirschner, MacMillan, New York, 1961.

[8] A. A. Schilt, *J. Amer. Chem. Soc.*, 1963, **85**, 904.

[9] G. Binsch and J. D. Roberts, *J. Phys. Chem.*, 1968, **72**, 4310.

[10] M. Brownstein and R. J. Gillespie, unpublished work.

n.m.r. spectrum of $HCNH^+$ reported by Olah and Kiorsky [5] in $HSO_3F–SbF_5$ solutions in our $HCN–HF–BF_3$ solutions at any temperature down to the freezing point. At −85 °C, the HCN resonance was still a single line, though slightly broader than that in the absence of BF_3. Evaporation of these solutions gave a small amount of an oily residue, which was not obtained from evaporation of either reactant in HF. This oil continually lost weight on evacuation of the vessel. We believe that this material was mainly $[HCNH^+][BF_4^-]$ which, because of the relatively weak acidity and high volatility of BF_3, easily dissociates according to (2).

In an attempt to obtain a more stable salt of $HCNH^+$, a solution of HCN and AsF_5 in HF was evaporated. A white solid was obtained, the weight of which corresponded very closely to that expected for quantitative formation of $HCNH^+AsF_6^-$, but this also slowly lost weight on evacuation of the vessel. The i.r. spectrum of this material had a broad band at 3200 cm^{-1}, which may be assigned to $\equiv C–H$ or $\equiv N–H$, and weak absorptions at 2100 and 2280 cm^{-1}, of which the former may be attributed to HCN and the latter to $–C\equiv N–$ in $HCNH^+$-AsF_6^-.

Polymerization of Hydrogen Cyanide in Solution in Hydrogen Fluoride.—Dove and Hallett [3] observed that the i.r. band of HCN in HF slowly decreased in intensity to be replaced by more complex absorptions; they found the half-life of this reaction to be about 40 h. We have made an n.m.r. and conductimetric study of this reaction. The ^{19}F n.m.r. spectrum, originally consisting of a single line from the solvent, slowly developed a broad doublet, J 59 Hz, in the fluorine-on-carbon region (Figure 2*a*). The broad doublet in the ^{19}F spectrum developed incompletely resolved fine structure when the sample was cooled to −85 °C (Figure 2*b*). Irradiating the ^{14}N nucleus at 4·4 MHz, while observing the ^{19}F spectrum at room temperature, gave the same result. From this we conclude that the broadness is due almost entirely to interaction of the fluorine atom with the quadrupolar ^{14}N nucleus and not to proton exchange. Figure 2*c* shows the room-temperature spectrum of the product arising from $HC^{15}N$. Not only are the lines narrow, but the double quartet is further split by interaction with the ^{15}N nucleus.

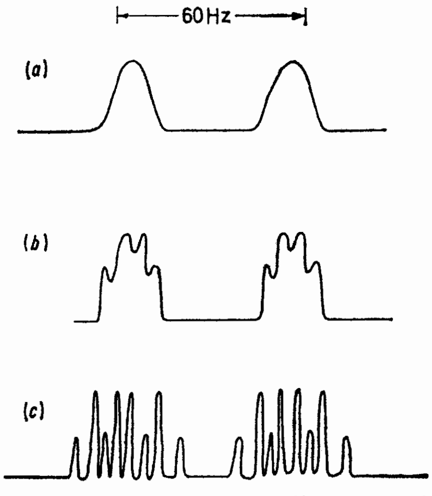

FIGURE 2 ^{19}F N.m.r. spectrum of $HC^{14}N$ in HF after 2 days: (*a*) at 20 °C; (*b*) at −80 °C or at 20 °C with ^{14}N decoupled; (*c*) as in (*a*) using $HC^{15}N$

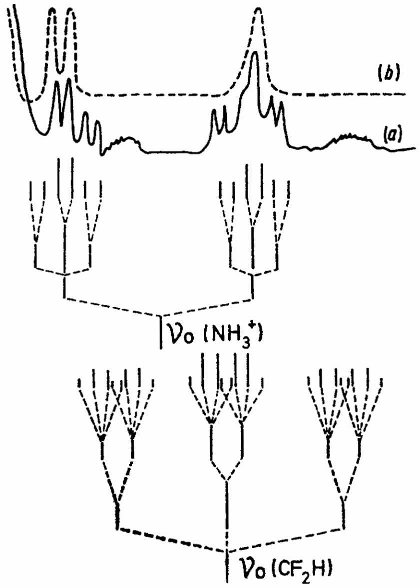

FIGURE 3 ^1H N.m.r. spectrum of $HC^{15}N$ in HF after 2 days: (*a*) normal spectrum; (*b*) with ^{19}F decoupled

The proton spectrum of the initial product from $HC^{14}N$ is dominated by a 1 : 2 : 1 triplet, J 58·7 Hz, which can be collapsed to a single absorption by irradiating the ^{19}F nuclei at 56·4 MHz; there is also a broad absorption which is due to protons bonded directly to the nitrogen atom. Attempts to resolve fine structure from this peak, by irradiating the ^{14}N nucleus, were not successful. This is not surprising since the one-bond coupling to the nitrogen atom would be expected to be large, thus requiring large radio-frequency power levels to effect complete decoupling. Solutions of $HC^{15}N$ in HF gave the spectrum shown in Figure 3*a* in which the line-widths were reduced and additional couplings can be seen. Decoupling of ^{19}F gave the simpler spectrum in Figure 3*b*. We assign these ^1H and ^{19}F spectra to the single species $F_2HC{\cdot}NH_3^+$. The variation of $J_{H–C–F}$ in systems of the type $F_2HC{\cdot}X$ is quite well documented: [11] J 54·5 (X = C); 55·8 ± 2 (S); 59·2 ± 2 (N); 74·0 ± 2 (O); and 81 Hz (F).

The fact that the coupling constant $J_{H\text{-}C\text{-}F}$ falls within the previously observed range for $F_2HC{\cdot}N$, together with the pronounced broadening effect of the ^{14}N nucleus, clearly establishes the $F_2HC{\cdot}N$ grouping. The quartet structure of the ^{19}F resonance shows that the nitrogen atom must carry three protons, thus defining the species as the difluoromethylammonium ion. This is confirmed in the proton spectrum of the ^{15}N species, which directly shows the NH_3^+ protons strongly split into a doublet by the nitrogen atom and

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[11] R. H. Arisan, T. Y. Sten, and N. R. Trenner, *J. Chem. Soc.*, 1962, 3828.

then into a triplet of doublets by the fluorine atoms and a single proton on the carbon atom, respectively. The coupling constants which characterize this spectrum are summarized in Table 2; we were unable to observe ^{13}C satellites.

TABLE 2

Coupling constants in $CF_2H{\cdot}NH_3^+$

	J/Hz		J/Hz
F–C–H	58·7	H–C–^{15}N	4·2
F–C–N–H	9·2	$^{15}NH_3^+$	75·4
F–C–^{15}N	13·8	$^{14}NH_3^+$	51 ± 2
H–C–N–H	3·0		

A solution of HCN in HF was set aside at room temperature for 3 days, cooled to −20 °C, and treated with AsF_5. A white crystalline precipitate was obtained which was recrystallized twice from HF at −80 °C and, when dissolved in SO_2, gave a poorly resolved proton-resonance spectrum (Figure 4). This showed the characteristic triplet of $CF_2H{\cdot}NH_3^+$ superimposed on a broad 1 : 1 : 1 triplet arising from coupling of the three N–H protons to the partially relaxed ^{14}N nucleus. The coupling constant, $J_{^{14}N-H}$ 51 Hz, agrees well with that calculated from the value given above for $J_{^{15}N-H}$. This spectrum showed an interesting temperature dependence. Increasing temperature decreased the rate of relaxation of the ^{14}N nucleus and hence sharpened the NH_3^+ absorption. On the other hand, the C–H proton, coupled much more weakly to the nitrogen atom, broadened with increasing temperature because of more rapid proton exchange, so that it is impossible to find a temperature at which all features are well resolved.

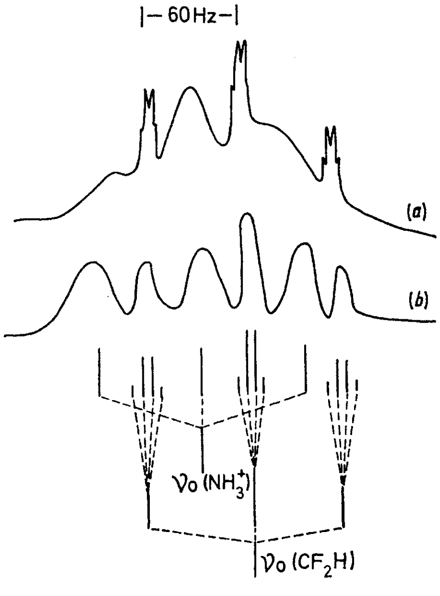

FIGURE 4 ^{1}H N.m.r. spectrum of $CF_2H{\cdot}NH_3^+AsF_6^-$ in SO_2: (a) −30 °C; (b) +30 °C

The i.r. spectrum of this air-sensitive solid was obtained from the powdered material between silver chloride plates over the range 4000—400 cm^{-1}. The observation of a broad absorption in the 3300 cm^{-1} region, the absence of a C≡N or C≡C stretching frequency and a sharp peak at 600 cm^{-1}, which may be attributed to AsF_6^-, confirm that this solid is $F_2HC{\cdot}NH_3^+AsF_6^-$. We believe this to be the first known example of a primary αα-difluoroamine derivative. These compounds are normally unstable to the elimination of HF.[12] Solutions of acetonitrile and pivalonitrile also appeared to add HF, but we made no attempt to identify the products in these cases. It would seem that this reaction might provide a general route to $RCF_2NH_3^+$ species, although the reaction of more concentrated solutions of nitriles in HF, leads only to the imido-fluoride compounds $RCF{=}\overset{+}{N}H_2\,F(HF)_n^-$ (R = alkyl group).[13]

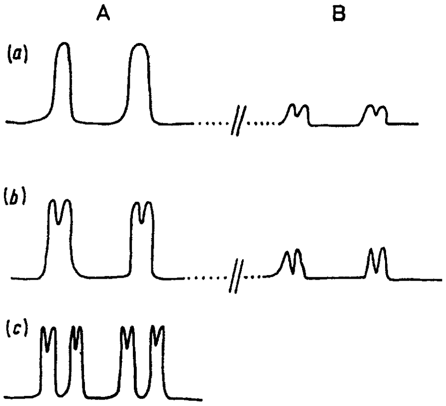

FIGURE 5 ^{19}F N.m.r. spectrum of aged solutions of HCN in HF: (a) at 20 °C; (b) at −80 °C or at 20 °C with ^{14}N decoupled; (c) as in (a) using $HC^{15}N$

The ^{19}F spectrum of $CF_2H{\cdot}NH_3^+$ gradually decayed to be replaced by two much sharper doublets, A and B, J 59 Hz (Figure 5a), the components of which showed a small doublet splitting (J 5 Hz) when the ^{14}N nucleus was irradiated (Figure 5b). The doublet B decayed further, and we conclude that the two doublets originate from different species. Substitution with ^{15}N introduced a further large splitting (Figure 5c). The proton resonance spectrum using ^{14}N is then two sets of triplets (J 59 Hz) of doublets (J 6 Hz), with a broad structureless absorption in the H-on-N region. This establishes the structure $F_2HC{\cdot}NH$–. The single proton on the nitrogen atom gives rise to the small doublet splitting in both the ^{1}H and ^{19}F spectra, the reduced symmetry of the ^{14}N environment resulting in more efficient quadrupole relaxation and, therefore, narrower lines. The ^{1}H spectrum from $HC^{15}N$ was too complex for further analysis. Clearly, these new species are a product of both addition of HF and polymerization.

The conductivity of a solution of sodium cyanide in HF was followed over a period of time in an attempt to determine the extent of polymerization. The initial conductivity was the same as that of an equimolar

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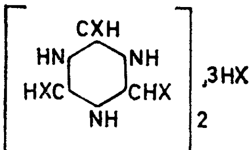
[12] R. E. Banks, 'Fluorocarbons and their Derivatives,' Oldbourne Press, London, 1962, p. 82.

[13] K. Weichert, H. H. Heilmann, and P. Mohr, *Z. Chem.*, 1963, **3** (**8**), 308.

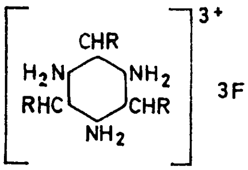
solution of sodium fluoride, as is expected from the non-basicity of HCN. The conductivity rose slowly due to the formation of $F_2HC{\cdot}NH_3^+$ and HF_2^-. After passing through a maximum after *ca.* 60 h, the conductivity slowly decreased and appeared to be constant after 1 week. The conductivity then corresponded to a solution in which the concentration of ions was 50% greater than that in the original solution, assuming that the mobility of the polymerized cation is the same as that of the sodium ion. We conclude that, during the polymerization, two HCN molecules give rise to one fluoride ion.

It has long been known that HCN reacts with the higher hydrogen halides to give 2HCN,3HX, which has been formulated as (I) or (II).[14,15] Our n.m.r. and conductivity results are incompatible with (I), and we have been unable to write any structures other than that of (II) or its polymers, presumably the trimer (III), to account for our results, including the unambiguous identification of the $CF_2H{\cdot}NH{-}$ group. The protonated amidine (II) can arise from addition of $CF_2H{\cdot}NH_2$ to HCN; (III) can arise from cyclisation of (II) or by addition of $CF_2H{\cdot}NH_2$ to 1,3,5-triazine resulting from the trimerization of HCN.[15,16]


(I)

$[CHX_2NHCH{=}NH_2]^+ X^-$

(II)


$3F^-$ (III); R = $CF_2H{\cdot}NH{-}$

Solutions of Silver(I) *Cyanide*.—After the commencement of the present work, Dove and Hallett[3] reported the results of their studies of solutions of silver(I) cyanide in anhydrous hydrogen fluoride. I.r. and n.m.r. spectroscopy and conductivity measurements led them to conclude that silver(I) cyanide behaves as a strong base, the protonated molecule being in equilibrium with $Ag[NCH]_2^+$ and Ag^+ [equation (3)]. We now report

$$2AgCN \overset{HF}{\rightleftharpoons} 2AgNCH^+ + 2F^- \rightleftharpoons Ag[NCH]_2^+ + Ag^+ + 2F^- \quad (3)$$

our own observations on this system which confirm some of Dove and Hallett's results and throw further light on the system.

A solution of silver cyanide in HF was titrated conductimetrically with BF_3 at 0 °C. The results are shown in Table 1 and Figure 6. The initial decrease in conductivity is due to conversion of the mobile fluoride ion to BF_4^-; precipitation which occurs approximately at the composition $BF_3 : AgCN = 0{\cdot}5 : 1$ then results in an increased gradient down to a sharp break at the 1 : 1 equivalence point. The absence of a further sharp rise up to the 1 : 2 equivalence point, which we did find in a separate experiment with sodium cyanide (Figure 6), confirms Dove and Hallett's conclusion that there is no free HCN in these solutions.

Dove and Hallett observed ^{13}C satellites in the proton n.m.r. spectrum of a solution of AgCN in HF showing that the ligand is indeed $H{-}C{\equiv}N{:}$, not $H{-}\overset{+}{N}{\equiv}\overset{-}{C}$, and that there is rapid exchange of HCN ligands between Ag^+ ions. We have observed the ^1H spectrum of ^{15}N labelled samples at temperatures down to −85 °C. The $^{15}N{-}H$ coupling constant was found to be very close to that (11·3 Hz) found in free $HC^{15}N$, thus confirming the $H{-}C{\equiv}N{-}Ag$ structure. The linewidth was narrower than that for the ^{14}N samples showing that the broadening of the resonance of the latter is due to the quadrupole moment of ^{14}N rather than slow exchange of HCN between different sites. Cooling to −85 °C produced no broadening, confirming that ligand exchange is very fast. Even after several months, there were no absorptions due to polymerization of HCN in HF and this is also true of a solution to which a little HCN had been added. This again supports the conclusion that the concentration of free HCN in silver(I) cyanide solutions is vanishingly small.

We found the ^{19}F n.m.r. spectrum of AgCN in HF to consist of a single line which was very much broader than that from the pure solvent. This width was unaffected by irradiation of the ^{14}N nucleus at 4·3 Hz; another, more concentrated, solution had a ^{19}F signal with a width of 145 Hz. In neither case were any further

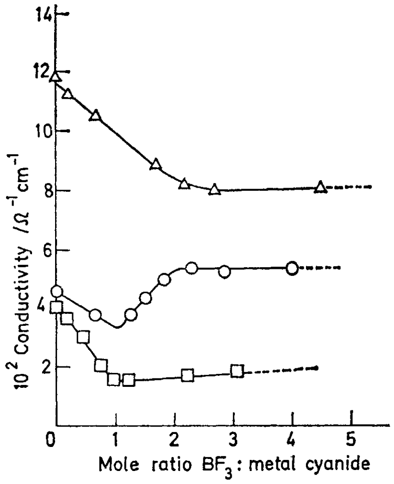


FIGURE 6 Conductimetric titration of metal cyanide complexes in anhydrous HF solution with BF_3 at 0 °C: (○), NaCN (0·190 mol kg^{-1}); (△), $H_4Fe(CN)_6$ (0·318 mol kg^{-1}); (□), AgCN (0·256 mol kg^{-1}). The AgCN data are displaced downwards by 2×10^{-2} Ω^{-1} cm^{-1} for clarity

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[14] C. Grundmann, *Angew. Chem. Internat. Edn.*, 1963, **2**(**6**), 309.

[15] E. Allenstein, A. Schmidt, and V. Beyl, *Chem. Ber.*, 1966, **99**, 431.

[16] C. Grundmann and A. Kreutzberger, *J. Amer. Chem. Soc.*, 1954, **76**, 5646.

absorptions seen at low temperatures. The ^{19}F resonance of $AgC^{15}N$ in HF was also broad. Solutions of fluoride ion in HF are well known to exhibit a single time-averaged ^{19}F resonance, but this is sharp. The sharpness of the ^{1}H signals of AgCN solutions precludes broadening from paramagnetic impurities and the double irradiation and ^{15}N experiments suggest that the width does not arise from interaction with the complexed cations.

We found solutions of AgF in HF to exhibit the same type of broad, single-line ^{19}F resonance and sharp ^{1}H resonance at all temperatures. This suggests that fluoride ion exchanges between AgF and HF at intermediate rates, but the linewidth did not appear to be a simple function of concentration. Although conductivity[17] and ebullioscopic[2] measurements have been unable to discern significant differences between AgF and KF solutions, Clifford[18] has assigned an ionization constant of 0·087 mol l^{-1} for AgF in HF on the basis of potentiometric measurements. Although this value appears to be rather low, our n.m.r. results do suggest an appreciable association of Ag^+ and F^- in HF. In conclusion, our findings confirm those of Dove and Hallett, but point to further weaker interactions in the system.

Solutions of Hexacyanoferric(II) *Acid.*—Hexacyanoferric(II) acid is soluble in HF to give pale yellow solutions having the conductivities shown in Table 3. The conductivities were almost twice those of solutions of potassium fluoride having the same concentration and were, in fact, very close to conductivities of solutions of calcium fluoride[10] in the same solvent. We conclude that hexacyanoferric(II) acid behaves as a strong 2 : 1 electrolyte. Three modes of ionization, therefore, seem plausible [equations (4)—(6)]. A conductimetric titra-

$$H_4Fe(CN)_6 \longrightarrow H_6Fe(CN)_6^{2+} + 2HF_2^- \quad (4)$$

$$H_4Fe(CN)_6 \longrightarrow H_4Fe(CN)_4^{2+} + 2HF_2^- + 2HCN \quad (5)$$

$$H_4Fe(CN)_6 \longrightarrow H_2Fe(CN)_6^{2-} + 2H_2F^+ \quad (6)$$

tion of the solution with BF_3 showed that the ionization produces HF_2^- not H_2F^+, since the conductivity decreased as BF_3 was added, reaching a minimum value at a mole ratio of $H_4Fe(CN)_6 : BF_3$ of 1 : 2. Thereafter, the conductivity remained constant within experimental error, even in the presence of a considerable excess of the Lewis acid. These results are shown in Figure 6 and Table 3. The initial decrease corresponds to the complexing of the highly conducting fluoride ion by BF_3 to form the less conducting BF_4^- ion. The magnitude of this decrease correlates well with that expected from the known conductivities of KF and KBF_4, and eliminates (6). The absence of a rise after $BF_3 : H_4Fe(CN)_6 = 2 : 1$, eliminates (5). Evaporation of the final solution gave a colourless solid, the weight of which approximated closely to that expected for quantitative formation of the product $Fe(CNH)_6,(BF_4)_2$. Continued evaporation resulted in a steady loss in weight which must indicate an appreciable dissociation pressure.

TABLE 3

Electrical conductivity of solutions of $H_4Fe(CN)_6$ in HF and conductimetric titration with BF_3

		$[H_4Fe(CN)_6] = 0·318$ mol kg^{-1}	
Molality / mol kg^{-1}	$10^2\kappa$ / Ω^{-1} cm^{-1}	Mole ratio $BF_3 : H_4Fe(CN)_6$	$10^2\kappa$ / Ω^{-1} cm^{-1}
0·012	0·78	0·0	11·8
0·018	1·10	0·17	11·4
0·025	1·44	0·71	10·5
0·039	2·13	1·68	8·76
0·050	2·66	2·21	8·15
0·064	3·20	2·73	8·01
0·099	4·58	2·88	8·20
0·148	6·60	4·46	8·10
0·318	11·8		
0·566	16·8		

$$[H_6Fe(CN)_6](BF_4)_2 \longrightarrow H_4Fe(CN)_6 + 2HF + 2BF_3 \quad (7)$$

The conclusion that no HCN is liberated in these solutions, is confirmed by the fact that it was impossible to observe any proton-resonance peaks other than that of the solvent at any temperature down to the freezing point at −84 °C, in contrast to the results obtained for solutions of sodium cyanide reported above. The absence of any peaks which could be assigned to the protonated hexacyanoferric(II) acid may be easily rationalized on the basis of rapid proton exchange between this species and the solvent. Furthermore, since the structure of the complex almost certainly involves bonding of the proton to the nitrogen atom of the cyano-group, one would expect a very broad proton-resonance absorption arising from strong coupling to the incompletely relaxed quadrupolar nitrogen nucleus. No change in the spectrum was observed, even after it had been kept for several months at room temperature, indicating that the complex is kinetically stable. It is noteworthy that, in aqueous acid solutions, HCN is liberated; that this does not occur in HF solution may be due to the poor ability of hydrogen fluoride to solvate Fe^{II}. It would thus appear that hexacyanoferric(II) acid is a strong dibase in anhydrous HF. This is not surprising in the light of the observed basicity of other cyano-species in mineral acids and the ability of this compound to act as a Lewis base to acceptors such as BF_3.

EXPERIMENTAL

Anhydrous HF was handled on a Monel and Kel-F vacuum line using n.m.r. and conductivity techniques as previously described.[19] Distilled HF, having a conductivity less than 1×10^{-4} Ω^{-1} cm^{-1}, was used for conductance measurements. $KC^{15}N$ (99%, Merk, Sharpe, and Dohm) contained traces of paramagnetic impurity which caused broadening of the n.m.r. spectrum. To prepare satis-

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factory samples, HF was condensed on to $KC^{15}N$ in a small Kel-F trap at −80 °C; all volatile species were then distilled into a Teflon n.m.r. tube and sealed. $AgC^{15}N$ was precipitated from neutral solution with the labelled potassium salt; it was free of the paramagnetic impurity. Hexacyanoferric(II) acid was prepared as the etherate [20] and handled in a dry nitrogen atmosphere. This material was decomposed to the free acid by evaporation in the conductance cell or n.m.r. tube. Silver(I) fluoride was prepared by evaporation of solutions of the oxide in aqueous HF. HF was condensed on to Ag_2O, the resulting colourless solution evaporated, and the remaining $AgHF_2$ warmed and the vessel evacuated to leave pure, dry AgF.

^{19}F and ^{1}H N.m.r. spectra were obtained on a Varian DP-60 instrument at 56·4 and 60·0 MHz, respectively. Double-resonance experiments were performed with an NMR Specialties accessory.

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